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Laminated Materials and Containers TherefromTechnical Field

This invention relates to laminated materials and to flexible containers formed from laminated materials, in particular thermoplastics laminates that include a layer of material having good vapour barrier properties.

Background of the Invention

Thermoplastics materials are widely used in packaging because of their low cost and ease of forming into a variety of shapes. However, most thermoplastics materials suffer from the disadvantage of providing only a relatively poor barrier to gases and vapours. Packaging having poor gas barrier properties is particularly disadvantageous for packaging oxygen-sensitive materials, such as foodstuffs, which are to be stored in a non-refrigerated condition. It is also disadvantageous for packaging to have poor vapour barrier properties when packaging items which are sensitive to moisture vapour, for example foodstuffs and confectionery which deteriorate when they become damp, and when packaging items which include flavouring components which diffuse through the packaging material with consequent loss of flavour.

Thermoplastic containers which are used for the storage and delivery of flavoured materials, e.g. toothpaste, are required to store the materials for prolonged periods of time, e.g. up to three years, without substantial loss of flavouring.

It has generally been thought that loss of flavouring is due to two mechanisms, namely permeation and absorption. The loss of flavouring due to permeation has been ameliorated by the use of laminates containing barrier layers. A known thermoplastics material with good barrier

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- 2 -

properties is ethylene vinyl alcohol (EVOH) which is typically used as a thin layer sandwiched between layers of other thermoplastics materials, typically polyolefinic materials. Other known materials with good barrier
5 properties to vapour transmission are polyamides, polyacrylonitrile and aliphatic polyketones, and aluminium foil.

A typical prior art laminate having a centrally positioned barrier layer is shown in Figure 1 which will be
10 described later.

Laminates having a barrier layer arranged asymmetrically within the different layers of the laminated material are also known. Figure 2, which will be described in detail later, shows a prior art laminate in which an EVOH
15 barrier layer is arranged towards the inside surface, in use, of the laminate. The provision of such a barrier layer appears to reduce the loss of flavourings from within the container.

However, EVOH and other barrier layers materials are
20 generally expensive and therefore a number of attempts have been made at improving the gas barrier properties of polyolefinic materials. GB-A-1136350, for example, proposes the use of circular plate-like fillers with a ratio of diameter to thickness of between 20:1 and 300:1 and a
25 diameter of at most 40 microns in polyolefin polymers selected from polyethylene, polypropylene, ethylene-containing copolymers containing at least 50 moles percent of ethylene, and polystyrene, the preferred amount of filler being from 0.1 to 50 wt% of the total weight of filled
30 polymer. Such filled polymer compositions have been proposed for the manufacture of films, for example films for food packaging.

US-A-3463350 is concerned with the production of moulded containers for packaging foodstuffs, the containers
35 being made from mixtures of high density polyethylene (HDPE)

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- 3 -

and mica particles, for example by compression or injection moulding. Such containers are said to reduce the discolouration of so-called canned corned beef as caused by oxygen compared with the use of similar containers made of HDPE filled with glass fibre or titanium dioxide instead of mica.

It has also been proposed in US-A-4528235 to incorporate platelet filler particles with an average equivalent diameter of from 1 to 8 microns, the maximum diameter being 25 microns, and a thickness of less than 0.5 microns, into HDPE having a melt index of from 0.01 to 1.0 g/10 minutes at 190°C as measured by ASTM D-1238 to produce films having a thickness of from 10 to 100 microns, with the intention of increasing the effectiveness of the barrier to oxygen of the films compared with films formed from unfilled HDPE.

In WO-A-96/17885, the contents of which are hereby incorporated into the present invention, there is proposed a moulding composition, and a method of making a moulding composition, for forming an article having increased barrier to gases and/or vapours, the method comprising the step of mixing together a substantially non-polar thermoplastics resin and a laminar filler, the laminar filler being capable of delaminating when the composition is subjected to high shear to increase the aspect ratio of the filler as it breaks down into platelets. WO-A-96/17885 further describes a composition containing 85 parts by weight of high density polyethylene and 15 parts by weight of talc that can be extruded in the form of a film or tube having increased barrier properties. The composition can be extruded as a single web, or can be co-extruded with other layers of material formed on one or other side of a core layer formed from the composition.

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Disclosure of the Invention

The object of the present invention is to provide a laminated material which is relatively cheap and which has improved resistance to the loss of flavour in goods stored in a container formed from the material.

According to one aspect of the present invention there is provided a method of reducing the absorbability of a laminated material used for the manufacture of flexible containers and which in use has an intended inner surface and an impermeable core barrier layer, comprising arranging for at least one further layer, formed from substantially non-polar thermoplastics resin or material filled with a platelet filler, to be positioned inwardly of the barrier layer.

The platelet filler can be any of a variety of lamellar fillers provided the platelets delaminate under shear when the filler is blended with the non-polar thermoplastics resin before processing and more particularly when the mixture of filler and thermoplastics resin is subjected to extrusion. Lamellar fillers include clays, mica, graphite, montmorillonite and talc.

Talc is a particularly preferred lamellar filler by virtue of its ease of delamination during shear. Talc, being a naturally occurring hydrated magnesium silicate, is available in a variety of grades of greater or lesser purity. It has been found that the ease of increasing the aspect ratio of talc when it is subjected to high shear in a non-polar thermoplastics resin appears to increase as the level of impurities within the talc decreases. Thus not only does it appear easier to delaminate the platelets of the talc, but the platelets themselves apparently resist fracture. Thus purer grades of talc are generally preferred since they lead to compositions which not only have good barrier properties but also have a high degree of whiteness

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- 5 -

without the necessity to include a white pigment such as titanium dioxide.

According to another aspect of the present invention, there is provided a laminated material for the manufacture of flexible containers and which, in use, has a surface intended to be external of the container and a surface intended to be internal of the container, the laminated material comprising an intermediate barrier layer of a thermoplastics material having, on its inner side, at least one further layer comprising substantially non-polar thermoplastics resin filled with platelet filler, preferably high purity talc.

The preferred non-polar thermoplastics resin is a polyolefin resin, for example a polymer derived from one or more aliphatic or aromatic alkylenes, e.g. a polymer containing units derived from at least one of ethylene, propylene, butylene, styrene, hexene and octene. The non-polar resin may also comprise a compound of one or more polymers as detailed below. Examples of specific polyolefin resins which can be used include polyethylene, polypropylene, ethylene/propylene copolymers, ethylene/propylene/butylene terpolymers, polyethylenes being particularly preferred by virtue of their good processing and welding characteristics. The polyethylene can be low density polyethylene, linear low density polyethylene (density of from 0.910 to 0.925 g.cm⁻³), medium density polyethylene, linear medium density polyethylene (density of from 0.925 to 0.950 g.cm⁻³), high density polyethylene (density of from 0.950 to 0.980 g.cm⁻³). High density polyethylene, or a compound of high density polyethylene and linear low density polyethylene, is particularly preferred by virtue of its higher inherent barrier properties compared with lower density polyethylenes.

The preferred HDPE resin has a density of at least 0.945 g.cm⁻³ and a melt flow index of from 4 to 10 g/10 min preferably 7 to 8 g/10 min, (2160 g load at 190°C) measured

- 6 -

to ISO/IEC 1133. A suitable material is available from DSM grade 9089F.

The barrier layer may comprise any of the known barrier materials such as EVOH, amorphous polyamides, aluminium foil, etc.

Particularly preferred grades of talc for use in the present invention are sold by Richard Baker Harrison Group, England under the Trade Mark MAGSIL, and an especially preferred grade is "Magsil Osmanthus" which delaminates in processing to form platelets having an average aspect ratio of from 16 to 30 and a minimum aspect ratio of 5.

Since the purity of talc is related to its whiteness, the preferred talc forms a moulded composition, as described below, having a CIE whiteness index of at least 40. These CIE (Commission Internationale d'Eclairage) whiteness index values are determined for compositions containing 15 percent by weight of talc in high density polyethylene with no other filler present, the determination being in reflectance mode with UV light included and specular reflection excluded, the observer angle being 10° of arc and the samples being backed by a white tile.

The talc is blended with the polyethylene in the weight ratio of 15 parts to 85 parts of polymer using a twin screw extruder or Banbury type mixer with a temperature profile ranging from 150°C to 220°C, the mixture being subjected to high shear during mixing, and then being extruded and cut into pellets. The pellets are then compression moulded to form plaques at a temperature of 150°C and pressure of 0.39 tonnes for 5 minutes.

The CIE whiteness index is measured using a Macbeth Spectrophotometer 2020+.

According to a further aspect of the present invention there is provided a container having flexible

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- 7 -

walls formed from a laminated material having a core barrier layer of a thermoplastics material with at least one further layer arranged internally of the barrier layer, said one further layer comprising substantially non-polar thermoplastics resin filled with platelets of talc having an aspect ratio of at least 5, an average aspect ratio of from 16 to 30 and a CIE whiteness of at least 40.

The arrangement of a layer of talc-filled non-polar thermoplastics resin internally of the barrier layer enables the thickness of the thermoplastics barrier layer to be reduced, from typically 25 microns, to a thickness of from 5 to 15 microns, preferably 10 microns, without substantially affecting the overall losses of volatiles from within the container. This is because the absorption properties of the container wall material are improved, that is less material is absorbed, whilst the permeation rate through the thinned down barrier layer remains largely unchanged.

The laminate construction can be a substantially symmetrical construction with the barrier layer at the centre and a layer comprising non-polar thermoplastics resin filled with platelet filler being arranged both inside and outside of the barrier layer. This allows the laminate to be used either way round which has advantages in the production of containers.

Preferably the thermoplastics barrier layer is an ethylene vinyl alcohol material or amorphous polyamide material. Preferably the talc filled non-polar thermoplastics resin layer has a thickness of from 5 to 150 microns, preferably from 10 to 70 microns, more preferably about 50 microns, and is spaced from the barrier layer only by a tie layer.

Preferably the talc filled non-polar thermoplastics resin layer is spaced from the internal surface of the laminate by an additional inner layer of a non-polar

09381385-020100

- 8 -

thermoplastics resin in order to improve the weld characteristics of the laminate on its inner surface. The additional inner layer may also contain said platelet filler, preferably talc. Preferably the further layer is formed from a high density polyethylene compound which may contain 15% by weight of talc filler, and at least a major, i.e. in excess of 50%, portion of high density polyethylene, and the additional layer is a linear medium density polyethylene. The further layer may alternatively comprise a tie layer which is filled with talc filler, especially when used in combination with aluminium foil. A typical tie layer for use with aluminium foil comprises ethylene acrylic acid copolymer having an acrylic acid content of from 2 to 10%.

15 Brief Description of Drawings

The invention will now be described, by way of example only, and with particular reference to the accompanying drawing, in which:-

Figure 1 and Figure 2 are schematic representations of prior art laminates;

Figure 3 is a schematic representation of both a control laminate and a first laminate according to the present invention; and

Figure 4 is a schematic representative of a second laminate according to the present invention.

Detailed Description of the Invention

Sample 1

A known laminate 11, illustrated in Figure 1, has an overall thickness T of about 300 microns and comprises a plurality of layers 12-20, the inner layer being identified layer 12 and the external layer being layer 20. The inner

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- 9 -

layer 12 comprises linear medium density polyethylene (LMDPE) having a thickness of about 75 microns, and the adjacent outer layer 13 comprises low density polyethylene (LDPE) having a thickness of about 20 microns. Externally of the layer 13 is a layer 14 of linear low density polyethylene (LLDPE) having a thickness of about 20 microns which is adhered to an ethylene vinyl alcohol (EVOH) barrier layer 16 (shaded for ease of identification) by a tie layer 15. The tie layer 15 typically comprises a maleic anhydride functionalised polyethylene of about 5 microns thickness and the barrier layer 16 has a thickness of about 25 microns.

Externally of the barrier layer 16 are a tie layer 17, a LLDPE layer 18 and a LDPE layer 19 which are substantially identical to the layers 15, 14 and 13, respectively. The external layer 20 is a layer of medium density polyethylene (HDPE) having a thickness of about 110 microns.

Sample 2

The second prior art laminate 21 shown in Figure 2 again has an overall thickness T of about 300 microns and comprises a plurality of layers 22-28, the inner layer being layer 22 and the external layer being layer 28. The inner layer 22 comprises LMPDE having a thickness of about 35 microns which is adhered to an EVOH barrier layer 24 (shaded for ease of identification) by a tie layer 23. The EVOH barrier layer 24 is about 15 microns thick and the tie layer 23 has a thickness of about 5 microns. Externally of the barrier layer 24 is another tie layer 25, a layer 26 of LLDPE having a thickness of 20 microns, a layer 27 of LLDPE or LDPE having a thickness of about 110 microns, and the external layer 28 of medium density polyethylene (MDPE) also having a thickness of about 110 microns.

With reference to Fig 3, there is shown a seven layer laminate 31 having an overall thickness of about 275 to 300 microns. This general laminate structure was used

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- 10 -

for a number of control samples 3-5, and a number of samples 6-13 according to the present invention. The laminate 31 from inside to outside comprises layers 32-38. The inner layer 32 is a layer of LMPDE about 25 to 35 microns thick.

5 The adjacent outer layer 33 is HDPE with a thickness of from 15 to 50 microns which is adhered to a barrier layer 35 by a tie layer 34. The barrier layer 35 is an EVOH layer or an amorphous polyamide layer. The barrier layer 35 is about 10 to 15 microns thick and the tie layer 34 has a thickness of

10 about 5 to 7.5 microns. Externally of the barrier layer 35 is a second tie layer 36, an outer HDPE layer 37 having a thickness of from about 50 to 190 microns, and an external LHPDE layer 38 having a thickness of about 25 to 35 microns.

The thickness in microns of the various layers for

15 each control sample is given in Table 1 below.

The samples 6-13 according to the present invention include layers of polymer filled with 15% ww talc (Magsil Osmonthous) arranged inside of the barrier layer 35. The structure of samples 6-13 are also given in Table 1

20 below with the layer thickness in microns.

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- 11 -

Table 1

	Control Samples			Samples according to the Invention							
	3	4	5	6	7	8	9	10	11	12	13
Layer 32	25	25	25	25	35	35	25	25	15	25	25
Layer 33	50	48	25	50*	15*	15*	15*	15*	20*	15*	25*
Layer 34	7.5	6	5	7.5	5	5	5	5	5	5	5
Layer 35	10**	15	15	10**	10**	10**	15	15	15	10	10
Layer 36	7.5	6	5	7.5	5	5	5	5	5	5	5
Layer 37	150	150	175	50*	145*	125*	185	185	200	165*	155
Layer 38	25	25	25	25	35	35	15	25'	15'	25'	25

* = 15% ww talc filled material

** = Amorphous polyamide basic layer

' = 1% ww talc filled material

15 Other laminates 41 according to the invention are shown in Fig 4 which shows a five layer laminate.

The laminate 41 comprises an inner layer 42 of talc filled LMDPE or HDPE, a tie layer 43, a barrier layer 44 of amorphous polyamide, an outer tie layer 45 and an outer
 20 layer of talc filled HDPE or LMPDE 46. The thicknesses in microns of the various layers for samples 14-17 according to the present invention are shown in Table 2 below.

09381385 020100

- 12 -

Table 2

Sample				
Layer	Sample 14	Sample 15	Sample 16	Sample 17
Layer 42	87* LMPDE	110* LMPDE	118* HDPE	166* HDPE
Layer 43	5	5	5	5
Layer 44	15	140	10	17
Layer 45	5	5	5	5
Layer 46	67* LMPDE	59* LMPDE	72* HDPE	155* HDPE

* 15% ww talc

Absorption Tests

The laminate material samples 1 to 17 were hermetically sealed across the mouths of 500 ml jars each containing a flavouring from the following: limonene, cineole, menthone and carvone. The mouths of the jars had a diameter of 48 mm to give an exposed area of laminate of 0.00181 m². The jars were maintained at a temperature of 25°C and at atmospheric pressure. The laminate samples were weighed periodically and the maximum absorption for all flavourings reached a substantially steady state after 7 days (168 hours).

The results of the tests for the prior art samples 1 and 2 are given in Table 3 below.

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- 13 -

Table 3

Absorption as weight (grams) gain per square meter after 7 days

Flavouring	Sample 1	Sample 2
limonene	9.4444	3.9444
cineole	8.5552	4.3332
menthone	5.3332	2.7220
carvone	1.7222	1.0000

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15 The results for samples 1 and 2 demonstrate that the placement of the barrier layer 24 closer to the inside surface of the laminate as in sample 2 is beneficial even though the thickness of the barrier layer 24 has been reduced in comparison to that of the barrier layer in sample 1, and the overall thickness of the laminate remains the same.

The results on the tests conducted on the samples of laminate constructed in accordance with Fig 3 are given below in Table 4.

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25 If the results for sample 3 are compared with results for sample 6 it can be seen that sample 6, which is a sample according to the invention, has unexpectedly good absorption properties in that the barrier layer 35 in sample 6 is spaced 82.5 microns from the internal surface of the laminate, which distance is identical to the spacing of the barrier layer 35 from the internal surface of the laminate

09381385-020100

- 14 -

of control sample 3. The improvement in absorption properties is due to the replacement of the HDPE layer 33, in sample 3, with the talc-filled HDPE layer of sample 7.

The talc-filled layer 33, which is inside the barrier layer 35, helps reduce the weight loss of flavouring due to absorption into the laminate. The talc-filled layer should be from between 5 to 150 microns in thickness, preferably from about 15 to 70 microns and more preferably about 50 microns in thickness. The talc-filled layer also tends to stiffen the laminate allowing a laminate of reduced overall thickness to be used whilst still maintaining a relatively stiff material.

Similarly, if the control sample 4 is compared with Sample 10 it can be seen that there is a marked decrease in flavour absorption due to the addition of talc to the inner HDPE layer 33 despite this layer being thinner in sample 10. A comparison between sample 5 and sample 13 shows a similar improvement on the absorption properties merely by adding talc to the inner HDPE layer 33.

A comparison between samples 10, 11 and 12 indicates that the absorption properties can be enhanced by including talc filler within the inner LMDPE layer 32.

A comparison between samples 9 and 12 would indicate that it is not critical whether the talc filler is included in the LMDPE inner layer 32 as in sample 12 or the HDPE inner layer 33 as in sample 9. The benefit is obtained by both constructions.

From samples 6, 13 and 9 it would be seen that the maximum benefits are obtained by keeping the talc filled HDPE inner layer down to a thickness of between 15-20 microns.

From samples 14-17 the absorption results are given in Table 5 below for a comparison between samples 15 and 16 the

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- 15 -

absorption properties are achieved by including the talc in HDPE rather than LMDPE, and that the inner layer containing the talc should be as thin as is possible for best reductions in absorption.

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Table 4

Absorption as weight (g) gain per square meter after 7 days

	Control Samples				Sample According to the Invention							
	Sample 3	Sample 4	Sample 5	Sample 6	Sample 7	Sample 8	Sample 9	Sample 10	Sample 11	Sample 12	Sample 13	
Flavouring												
limonene	11.2220	6.7600	4.2200	5.3880	3.9440	3.8320	3.1120	3.500	2.6680	3.2760	3.6640	
cineole	9.9444	5.8800	3.7760	4.5560	3.5560	3.4440	3.0880	3.000	2.3880	2.7240	3.3888	
menthone	7.2776	4.5600	2.5520	3.5560	2.2760	2.2240	1.7240	1.8320	1.5480	1.6680	2.0520	
carvone	4.8332	2.440	1.6640	2.6120	1.4440	1.3320	1.2240	1.1120	1.1680	1.1680	1.9440	

Table 5

Absorption as weight (g) gain per square meter after 7 days

Samples of Second Embodiment				
flavouring	Sample 14	Sample 15	Sample 16	Sample 17
limonene	6.28	8.84	4.84	7.88
cineole	5.12	7.60	4.44	5.88
menthone	3.32	5.88	2.96	5.28
carvone	2.32	4.60	2.28	3.88

The laminate construction including the single layer 42 of talc filled HDPE on the inside of the barrier layer 44 has absorption properties that are improved over the contract sample 3 which has a similar thickness of non-polar polyethylene layer inside of an amorphous polyamide barrier layer.

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